In situ Determination of SCR Catalyst Activity

R. Smith, Presenter
Fossil Energy Research Corporation
23342-C South Pointe Dr, Laguna Hills, CA 92653
E-mail: rsmith@ferco.com Telephone: (949) 859-4466

Co-authors:

L. Muzio
Fossil Energy Research Corporation

K. Harrison
Southern Company Generation
P.O. Box 2641 Bin 14N-8195, Birmingham, AL 35291
E-mail: keharris@southernco.com Telephone: (205) 257-6832

D. Broske
Electric Power Research Institute
1300 West W. T. Harris Blvd, Charlotte, NC 28262
E-mail: dbroske@epri.com Telephone: (704) 595-2255

C. Miller
US DOE/NETL
626 Cochrans Mill Road, Pittsburgh, PA 15236
E-mail: charles.miller@netl.doe.gov Telephone: (412) 386-5745

Summary

With more than 100 GW of selective catalytic NO_x reduction (SCR) installed on coal-fired utility boilers, U. S. utilities are entering a period where catalyst management is becoming an important activity. When an SCR system is initially designed and built an excess of catalyst activity is installed in the reactor. With increasing operating hours the catalyst activity will degrade and some of the catalyst surface will plug with fly ash. Both of these will lead to decreasing performance of the SCR system. At some point it will be necessary to either add catalyst or replace a portion of the used material with fresh catalyst.

A measure of the overall activity of an SCR system is the "Reactor Potential". The reactor potential is the catalyst activity multiplied by the total catalyst surface area per unit flue gas:

$$RP = \sum_{layers_i} K_i \frac{A_{cat_i}}{Q_{fg}} = \sum_{layers_i} K_i / Av_i \qquad \text{Eq. (1)}$$

K_i = Catalyst activity of the i^{th} layer

A_{cat_i} = Total Surface area of the i^{th} layer

Q_{fg} = Flue gas flowrate

Av_i = Area Velocity of the i^{th} layer

Since some of the surface area will be lost due to plugging by flyash, equation (1) is modified to account for the blockage.

$$RP = \sum_{layers_i} K_i \; A_{cat_i}^{clean} \left(1 - B_i\right) / Q_{fg}$$

$$= \sum_{layers_i} K_i \left(1 - B_i\right) / Av_i^{clean} \qquad \text{Eq. (2)}$$

$A_{cat_i}^{clean}$ = Total surface area of the i^{th} layer without blockage

B_i = Fraction of the catalyst channels on the i^{th} layer that are blocked

Av_i^{clean} = Area velocity of the i^{th} layer without blockage

Traditionally, in order to determine the reactor potential a utility will 1) remove a sample of catalyst from each layer of the reactor and send it to a laboratory, 2) the laboratory will be conduct a test to determine the activity (K_i), and 3) a visual inspection of the reactor will be completed to estimate the blockage in each layer (B_i). With this information the reactor potential will be calculated using equation (2). Utilizing this method, the reactor potential calculation is only as accurate as the blockage estimation.

Currently, most utilities operate their SCR systems only during the five-month ozone season. The seven-month non-operating season provides plenty of time to obtain catalyst samples, send them out for testing, and receive the activity results prior to the next ozone season. However, this still only represents one data point per layer, per year. As utilities move to year-round operation of their SCR systems and major outages are stretched from 18 to 36 months, there will be less opportunity to obtain physical catalyst samples.

Fossil Energy Research Corp (FERCo) has developed a new device (patent pending) that allows the reactor potential and catalyst activity to be determined *in situ*. With this new approach to catalyst testing, the reactor potential and activity can be measured at any time, independent of unit outages. With multiple devices, each layer can be measured independently and a number of individual measurements can be made across a given catalyst layer.

Unlike the laboratory approach that measures the activity K, and then uses the design area velocity and an estimate of the blockage to calculate the reactor potential, this new device provides a direct measurement of reactor potential. The *in situ* measurement technique is similar to the laboratory measurement. A small auxiliary ammonia injection grid (AIG) is located above the section of catalyst to be tested. To make the measurement, ammonia is added such that the local NH_3/NO_x ratio exceeds 1.0. The NO_x reduction is measured, and then the reactor potential for each layer is calculated from the following equation:

$$RP_i = -\ln(1 - \Delta NO_{xi}) \quad \text{Eq. (3)}$$

In equation (3) above, RP_i and ΔNO_{xi} are the reactor potential and NO_x removal for each layer. If the activity K_i is needed, then equation (2) can be used to calculate the activity (note this requires an estimate of the blockage for each layer).

FERCo is currently conducting a field test of a prototype *in situ* activity measurement system for ultimate commercial application. This project is one of the Advanced NO_x Control Projects in the DOE/NETL Innovations for Existing Plants Program, with funding being provided by the DOE, EPRI, and Southern Company. The host site for the project is Alabama Power Company's Gorgas Unit 10. The Unit 10 SCR is a two-reactor design with a 3 + 1 layer configuration that started operation in 2002. Prior to the 2005 ozone season, three *in situ* devices were installed, one on each of the three catalyst layers in one of the two reactors. Six sets of activity measurements were made throughout the ozone season at nominal four-week intervals. The decay in reactor potential can be characterized by the relative reactor potential, RP_i/RP_{io}, which normalizes the reactor potential of the catalyst layer at a particular point in time to that for the fresh, unexposed catalyst layer (RP_{io}). At the start of the 2005 ozone season, RP_i/RP_{io} was found to be 0.60, 0.67, and 0.77 for Layers 1, 2, and 3, respectively. The timing of these tests corresponded to the start of the fourth ozone season of operation (nominally 11,500 operating hours). At the end of the 2005 ozone season the relative reactor potential values from the *in situ* measurements were found to be 0.47, 0.59, and 0.73 for Layers 1, 2, and 3, respectively. The results from the 2005 ozone season demonstration clearly showed the advantage of having more than one data point per year in defining the catalyst deactivation curve.

To compare the results of the *in situ* technique to the laboratory measurements, the laboratory activity values (K_i) were used along with Southern Company's estimate of blockage for each layer and the design area velocity to calculate the reactor potential of each layer. While there was a general agreement between the two techniques for determining reactor potential, there were also some differences. These differences could be due to 1) the estimate of the blockage needed by the laboratory technique 2) spatial variations in activity across a layer, 3) differences in the actual flue gas flow rate compared to the design flow rate, or 4) the NH_3/NO_x ratio used in the test ($NH_3/NO_{x\ lab} = 1.0$ versus $NH_3/NO_{x\ in\ situ} > 1.0$).

The field test program will continue through the 2006 ozone season, with a second *in situ* device is being added to each of the three catalyst layers originally installed in the reactor. Additionally, two *in situ* devices will be added to a new fourth layer of catalyst (installed prior to the 2006 ozone season), for a total of eight devices overall.